Permeation of Methylethylketone, Oxygen and Water Vapor through PET Films Coated with SiO$_x$: Effect of Temperature and Coating Speed

Gavriil D. DIMITROULAS, Anastasia B. BADEKA, and Michael G. KONTOMINAS[†]

Laboratory of Food Chemistry and Technology, Department of Chemistry, University of Ioannina, Ioannina-45110, Greece

ABSTRACT: The permeation parameters of commercial poly(ethylene terephthalate) (PET) films, PET films coated with SiO$_x$ and SiO$_x$-coated PET films laminated onto low density polyethylene (LDPE) film were determined for methylethylketone (MEK) at 25 °C, 35 °C and 45 °C using the permeation cell/gas chromatography method. Permeation of O$_2$ and water vapor were also determined to monitor overall changes in the barrier properties of the experimental films. Results showed that the SiO$_x$ coating increased the film barrier to MEK by 7–8 times at 25 °C. The barrier to oxygen and water vapor increased by 40 and 7–8 times respectively after coating at the same temperature. Increase in temperature by 10 °C resulted in a ten fold increase in permeation rate of MEK and a two fold increase in oxygen and water vapor permeation rate. Permeation values showed slight variation indicating the need for further development and standardization of the SiO$_x$ web coating process. The web coating speed did not seem to influence the barrier properties of the films. Permeation coefficient, diffusion coefficient, solubility coefficient and activation energy values for permeation were calculated for all samples.
     KEY WORDS   Permeation / SiO$_x$-coated PET / Methylethylketone /

Barrier properties of plastics to gases (O$_2$, CO$_2$, N$_2$), water vapor and organic vapors are of utmost importance in food packaging applications where the packaged product's sensitivity to oxygen, water vapor and loss or pick up of odorous compounds determines product quality and shelf life. Such food packaging applications include snacks, dried soups and sauces, edible fats, coffee and baked goods but also lightly processed meat and fish packaged under modified atmospheres.[1–5]

The permeation properties of polymer packaging materials are influenced by (a) compositional variables such as chemical composition of the packaging material and permeant, morphology of the polymer, concentration of the permeant, presence of co-permeant and (b) environmental and geometric factors such as temperature, light, relative humidity and packaging geometry. All these factors must be taken into account when designing a particular package system.[6]

Whereas extensive work has been carried out on permeation of gases and water vapor through polymeric packaging materials, permeation data on volatile organic compounds are rather limited.[5,7–11] Even more scarce is data on the effect of environmental factors (temperature and relative humidity) on the permeation of organic vapors through plastics packaging materials.[12–15]

Contemporary high barrier flexible packaging materials include laminated, coextruded and aluminum-coated structures using vacuum-coating techniques.

Recently transparent flexible high barrier packaging materials have been developed based on SiO$_x$ deposition on films such as poly(ethylene terephthalate) PET, oriented polypropylene (OPP) and oriented polyamide (OPA).[5,16–18] Typically, SiO is sublimed from the solid state and the SiO vapor is oxidized in a controlled reactive atmosphere to achieve a degree of oxidation between 1.5–1.7. The resulting SiO$_x$ coating of thickness ~8 × 10^{-6} cm consists of a mixture of SiO (silicon monoxide), Si$_2$O$_3$ (disilicon trioxide) and SiO$_2$ (silicon dioxide) and therefore has a slightly yellowish appearance.[16] SiO$_x$-coated plastics have a number of advantages over conventional aluminum coated ones including transparency, retortability, microwaveability and the fact that they are not influenced by humidity.[16,19]

The objectives of the present work were to determine (a) the permeation parameters of experimentally produced SiO$_x$-coated PET films to methylethylketone (MEK) (b) the effect of coating speed on barrier properties of above films and (c) the effect of temperature on the permeation of MEK through SiO$_x$-coated PET film.

Methylethylketone was chosen as a model compound because of its relatively low molecular weight and its routine use in converting processes as an adhesive and/or ink solvent.

EXPERIMENTAL

Materials

Commercial Melinex 800 PET film, 1.2×10^{-3} cm in thickness and 30 cm in width was used in all experiments. SiO_x-coated PET films at coating speeds of 2×10^2 and 4×10^2 cm s^{-1} (higher coating speed corresponds to a thinner layer of SiO_x deposited on the PET surface), as well as SiO_x-coated PET films laminated to LDPE 5×10^{-3} cm in thickness were provided by various converting companies that participated in the project. SiO_x deposition was achieved on a Leybold A.G. (Hanau, Germany) laboratory scale vacuum metallizing unit operating at pressure of 4×10^{-4} mbar and a temperature of 1500 °C.

All measurements run on SiO_x-coated and coated/laminated PET films were also made on the base (PET) film which was taken as the control sample. Methylethylketone, analytical grade was purchased from Merck, D-6100, Darmstadt, Germany and used in all permeation experiments. Mineral oil purchased from Tudapetrol, Germany was used to dilute the methylethylketone so as to achieve a sufficiently low vapor pressure, which would correspond to actual vapor pressure values encountered in packaged food products.

Methods

a) Permeation to Methylethylketone

Circular film samples (area: 50.24 cm^2) were mounted to permeation cells (Figure 1) between upper and lower compartments. Given that film samples were heterogeneous in nature including conventional PET, SiO_x-coated PET and SiO_x-coated PET laminated to LDPE (PET–SiO_x//LDPE), mounting of the film samples was such that the PET side of the structure was always facing the cell lower compartment. Volume of upper compartment was 55 cm^3 and of lower compartment was 140 cm^3. Cells were equipped with Viton-O rings made of a fluorocarbon elastomer and teflon coated septa to avoid organic vapor sorption/
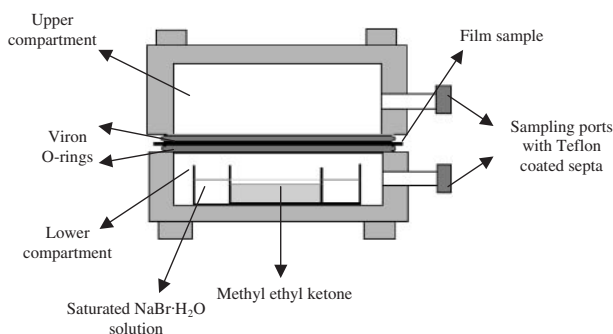

Figure 1. Cross sectional view of a permeation cell.

swelling phenomena. A glass Petri dish, 5 cm in diameter, containing methylethylketone was placed within a second Petri, dish 8 cm in diameter, containing a saturated NaBr·2H$_2$O solution providing a RH of 58 ± 2% to the lower compartment of the cell. Cells were sealed, upper compartment was flushed with N$_2$ and kept in a model WTB, Binder environmental chamber at temperatures $T = 25$, 35 and 45 ± 1 °C. Operational temperature range of the environmental chamber was 4–100 °C (tolerance ± 1 °C). At predetermined time intervals gas samples (volume 0.5 cm^3) were collected from the sampling ports using a gas tight syringe and injected into a Gas Chromatograph (GC) with flame ionization detection. To maintain a constant, total pressure in the low concentration cell compartment, the volume of headspace gas removed for analysis was replaced with an equal volume of nitrogen. The quantity of vapor permeated with time was monitored until a steady state rate of diffusion was obtained. The driving force for diffusion was determined by sampling the high concentration cell compartment and using the procedure described above.

In contrast to evaporated aluminum which has a microcrystalline structure and permeation of penetrant proceeds through "pin windows" or small uncoated surfaces on the PET layer, SiO_x is deposited as a glassy continuous network and is therefore totally amorphous. Permeation in this case proceeds through "activated" diffusion through the SiO_x layer.

Chromatographic Conditions A Hewlett Packard model 5890 GC equipped with a flame ionization detector was used in all tests.

The column used was HP-5 (Crosslinked 5% PH ME Siloxane) 30 m × 0.32 mm × 0.25 µm film thickness. Operational temperatures were: Column temperature: 130 °C, Injection port temperature: 150 °C, Detector temperature: 250 °C.

b) Permeation to Oxygen and Water Vapor

For the determination of permeation rates of O$_2$ and water vapor through the samples, the Mocon Oxtran 2/20 and Permatran 3/31 permeability testers were used, based on coulometric and IR detection respectively. Measurements for O$_2$ were made at RH = 58 ± 1%. Measurements for water vapor were made at RH = 100%. Temperature in all experiments varied between 25 °C and 45 °C.

c) Thickness of the SiO_x coatings was determined on cross fractures of coated films, prepared under liquid N$_2$ using a scanning electron microscope (JOEL, model JSM-5600). Since the nominal resolution of the instrument is 5 nm the film layer thickness was also determined by X-Ray fluorescence (XRF) spectroscopy using an ASOMA model 200/400 benchtop unit
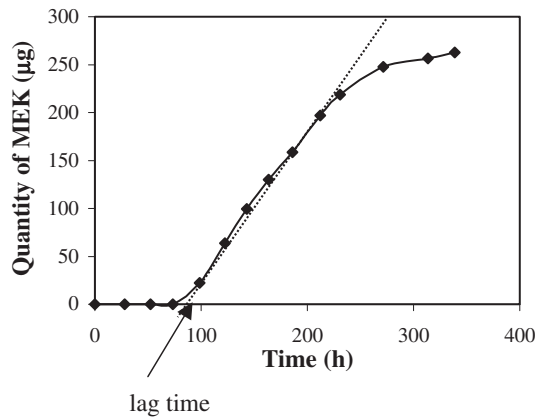
Figure 2. Determination of lag time for SiO$_x$-coated PET// LDPE film (coating speed 2×10^2 cm s^{-1}).

(Munich, Germany). SEM was also used to produce surface micrographs of the SiO$_x$ coating on PET films.

RESULTS AND DISCUSSION

Permeation to Methylethylketone

The amount of MEK permeated through the film at a given time was determined based on Fick's law equation as described by Adamantiadi *et al.* (2001).[5]

A plot of the increase of methylethylketone in the upper compartment as a function of time resulted in the permeation curve (Figure 2).

The slope of the steady state portion was determined and used in combination with the film specimen surface area and thickness to calculate the permeation rate and permeation constant using Eqs 1 and 2:

$$\frac{\Delta Q}{\Delta t} = \frac{s}{A} \tag{1}$$

$$P = \frac{s \cdot l}{A \cdot \Delta p} \tag{2}$$

where $\Delta Q / \Delta t$ is the permeation rate (10^{-3} g cm^{-2} s^{-1}), s is the slope of steady state portion of permeation curve (10^{-3} g s^{-1}), l is the film thickness (0.0012 cm), A is the surface area of film (50.24 cm^2), Δp is the driving force (atm) and P is the permeation constant of permeant in film (10^{-3} g cm^{-1} s^{-1} atm^{-1}).

Equation 3 was used to calculate the diffusion coefficient of the permeant in the film assuming that the film is initially free of permeant and the receiving volume of the test cell is maintained at essentially zero concentration of permeant:[20]

$$D = \frac{l^2}{6\theta} \tag{3}$$

where D is the diffusion coefficient (cm^2 s^{-1}) and θ is the lag time (s). The lag time was obtained experimen-

tally as the intercept on the time axis of the steady state portion of the permeation curve (Figure 2).

The solubility coefficient S (10^{-3} g cm^{-3}) of the permeant in the film was determined by substitution into Eq 4:

$$P = D \cdot S \tag{4}$$

Of course the basic assumption for calculation of above diffusion coefficient (D) and solubility coefficient (S) values is that films are homogeneous in nature. For films coated with SiO$_x$ Eqs 3–5 do not hold and give apparent D and S.

The temperature dependency of the permeation rate can be expressed by Eq 5:

$$P = P_0 \exp\left(\frac{-E_A}{RT}\right) \tag{5}$$

where P_0 is a constant, E_A is the activation energy for permeation, R is the gas constant and T is the absolute temperature.

Initial experiments involving a 50 % dilution of methylethylketone with mineral oil gave no measurable permeation data after 3.88×10^6 s (1.5 months) and were thus discontinued. All further experiments were run using 100 % methylethylketone as the permeant.

Table I gives permeation rate, lag time, permeation constant, diffusion coefficient and solubility coefficient of conventional PET, SiO$_x$-coated PET and SiO$_x$-coated PET films laminated to LDPE at 25 °C and coating speeds 2×10^2 and 4×10^2 cm s^{-1}. Another reason for characterizing diffusion coefficients and solubility coefficients as $D_{apparent}$ and $S_{apparent}$ is that D and S have no physical meaning for multilayer materials. The calculation of $D_{multilayer}$ and $S_{multilayer}$ would require isolation of the PET from the SiO$_x$ layer and calculation of D and S for each substrate separately.

Based on an average permeation rate of 69.5×10^{-11} g cm^{-2} s^{-1} for uncoated PET film versus an average of 9.5×10^{-11} g cm^{-2} s^{-1} for SiO$_x$ coated PET film one easily establishes an increase in barrier properties of the latter by a factor of ~7 to 8 times. A respective increase in lag time was observed from 85.5×10^3 s (24 h) for the uncoated film to 268×10^3 s (74.5 h) for the SiO$_x$-coated film.

Slight variation in permeation rate observed for the SiO$_x$-coated films can be accounted for, assuming the existence of small cracks on the surface of the SiO$_x$ layer giving rise to a random local increase in permeation rate. It has been postulated by Sajiki (1991) that the barrier properties of the silica-coated PET film are governed by defects, non-homogeneity of both the surface coating thickness and composition or preferential diffusion paths, all of which can contribute to

the observed permeability. SEM image analysis of the surface of the SiO$_x$ coating (data not shown) supports this assumption showing irregular cracks and local fractures of the SiO$_x$ layer.

The permeation rates of the SiO$_x$-coated PET are of the same order of magnitude with those of the SiO$_x$-coated PET, laminated to LDPE. Such a trend is expected since LDPE is known to be a poor barrier to fixed gases (O$_2$, N$_2$, CO$_2$) and organic vapors. Respective lag times increase from 268×10^3 s (74.5 h) to 288×10^3 s (80 h), reflecting the additional amount of time required for the MEK vapor to penetrate the LDPE layer. Coating speed (2×10^2 cm s^{-1} *vs.* 4×10^2 cm s^{-1}) and corresponding SiO$_x$ layer thickness do not seem to affect, under present experimental conditions, the barrier properties of the coated films. This is in general agreement with data of Krug and Rübsam (1990b) according to which a SiO$_x$ layer thickness of $\geq 5 \times 10^{-6}$ cm does not affect the permeability of SiO$_x$-coated PET film structures.

The diffusion coefficient is a measure of how rapidly penetrant molecules are advancing through the polymer barrier (kinetic parameter), while the solubility coefficient describes the amount of the penetrant molecule dissolved in the film at equilibrium conditions (thermodynamic parameter).

Permeation constants decreased by ~8 times after coating of the PET film with SiO$_x$. Diffusion coefficients slightly decreased (by 3 times) but remained within the same order of magnitude with those of the uncoated PET samples. This indicates that the permeation process is partly controlled by diffusion through the PET layer and partly by diffusion through the silica coating on the polymer.

Solubility coefficients slightly decreased (by 2–3 times) reflecting the decreased amount of MEK dissolved in the SiO$_x$ layer as compared to the PET layer. Based on very low D and high S parameters (Table I) a permeation mechanism controlled purely by diffusion of the penetrant through the composite structure is suggested. In practice, when dealing with packaging films of the same permeability, the film possessing a solubility (S) controlled permeation mechanism would be preferable due to a lower flavor absorption (flavor scalping).

Tables II and III present respective permeation data at 35 and 45 °C. Based on an average permeation rate of 20.0×10^{-10} g cm^{-2} s^{-1} for uncoated PET film ver-

Table I. Permeation parameters of PET, SiO$_x$-coated PET and SiO$_x$-coated PET//LDPE films as a function coating speed at 25 °C

Material	CS (10^2 cm s^{-1})	SiO$_x$ LT (10^{-6} cm)	$\Delta Q/\Delta t = s/A$ (10^{-11} g cm^{-2} s^{-1})	LT (10^3 s)	P (10^{-13} g cm^{-1} s^{-1}*720 ppm)	$D_{apparent}$ (10^{-13} cm^2 s^{-1})	$S_{apparent}$ (10^{-1} g cm^{-3}*720 ppm)
uncoated PET	—	—	69.5[a] $\pm$ 5.5[b]	85.5 $\pm$ 7.4	8.3 $\pm$ 0.6	28.1 $\pm$ 2.4	3.0 $\pm$ 0.3
PET–SiO$_x$	2	8.4–9.6	9.1 $\pm$ 0.7	263 $\pm$ 19.1	1.1 $\pm$ 0.1	9.1 $\pm$ 0.8	1.1 $\pm$ 0.1
PET–SiO$_x$	4	4.6–5.6	9.9 $\pm$ 0.9	274 $\pm$ 24.0	1.2 $\pm$ 0.1	8.8 $\pm$ 0.6	1.4 $\pm$ 0.1
PET–SiO$_x$//LDPE	2	8.4–9.6	7.6 $\pm$ 0.4	279 $\pm$ 28.1	0.9 $\pm$ 0.1	8.6 $\pm$ 0.5	1.1 $\pm$ 0.1
PET–SiO$_x$//LDPE	4	4.6–5.6	7.0 $\pm$ 0.6	297 $\pm$ 22.5	0.8 $\pm$ 0.1	8.1 $\pm$ 0.4	1.1 $\pm$ 0.1

// = laminated   CS = coating speed   SiO$_x$ LT = SiO$_x$ layer thickness $\Delta Q/\Delta t$ = permeation rate   LT = lag time P = permeation coefficient D = diffusion coefficient S = solubility coefficient   [a]each value is the mean of four measurements ($n = 4$)   [b] SD value.

Table II. Permeation parameters of PET, SiO$_x$-coated PET and SiO$_x$-coated PET//LDPE films as a function coating speed at 35 °C

Material	CS (10^2 cm s^{-1})	SiO$_x$ LT (10^{-6} cm)	$\Delta Q/\Delta t = s/A$ (10^{-10} g cm^{-2} s^{-1})	LT (10^3 s)	P (10^{-13} g cm^{-1} s^{-1}*720 ppm)	$D_{apparent}$ (10^{-12} cm^2 s^{-1})	$S_{apparent}$ (10^{-1} g cm^{-3}*720 ppm)
uncoated PET	—	—	20.0[a] $\pm$ 1.8[b]	47.3 $\pm$ 3.6	24.0 $\pm$ 1.8	5.1 $\pm$ 0.4	4.7 $\pm$ 0.3
PET–SiO$_x$	2	8.4–9.6	7.8 $\pm$ 0.6	86.4 $\pm$ 6.1	4.0 $\pm$ 0.3	2.8 $\pm$ 0.2	1.2 $\pm$ 0.1
PET–SiO$_x$	4	4.6–5.6	7.3 $\pm$ 0.5	89.1 $\pm$ 9.0	4.0 $\pm$ 0.4	2.7 $\pm$ 0.2	1.2 $\pm$ 0.1
PET–SiO$_x$//LDPE	2	8.4–9.6	7.2 $\pm$ 0.5	92.3 $\pm$ 8.8	3.3 $\pm$ 0.3	2.6 $\pm$ 0.3	1.0 $\pm$ 0.1
PET–SiO$_x$//LDPE	4	4.6–5.6	7.6 $\pm$ 0.5	94.7 $\pm$ 8.6	3.1 $\pm$ 0.2	2.5 $\pm$ 0.3	1.0 $\pm$ 0.1

// = laminated   CS = coating speed   SiO$_x$ LT = SiO$_x$ layer thickness $\Delta Q/\Delta t$ = permeation rate   LT = lag time P = permeation coefficient D = diffusion coefficient S = solubility coefficient   [a]each value is the mean of four measurements ($n = 4$)   [b] SD value.

Table III. Permeation parameters of PET, SiO$_x$-coated PET and SiO$_x$-coated PET//LDPE films as a function coating speed at 45 °C

Material	CS (10^2 cm s^{-1})	SiO$_x$ LT (10^{-6} cm)	$\Delta Q/\Delta t = s/A$ (10^{-9} g cm^{-2} s^{-1})	LT (10^3 s)	P (10^{-12} g cm^{-1} s^{-1}*720 ppm)	$D_{apparent}$ (10^{-11} cm^2 s^{-1})	$S_{apparent}$ (10^{-1} g cm^{-3}*720 ppm)
uncoated PET	—	—	61.5[a] $\pm$ 4.1[b]	18.2 $\pm$ 1.6	73.8 $\pm$ 6.8	1.3 $\pm$ 0.1	5.9 $\pm$ 0.4
PET–SiO$_x$	2	8.4–9.6	3.2 $\pm$ 0.3	23.6 $\pm$ 1.9	3.8 $\pm$ 0.3	1.0 $\pm$ 0.1	3.8 $\pm$ 0.3
PET–SiO$_x$	4	4.6–5.6	2.4 $\pm$ 0.2	23.0 $\pm$ 1.8	2.9 $\pm$ 0.3	1.0 $\pm$ 0.1	2.8 $\pm$ 0.3
PET–SiO$_x$//LDPE	2	8.4–9.6	2.0 $\pm$ 0.2	24.7 $\pm$ 2.1	2.4 $\pm$ 0.2	1.0 $\pm$ 0.1	2.4 $\pm$ 0.2
PET–SiO$_x$//LDPE	4	4.6–5.6	2.1 $\pm$ 0.2	25.2 $\pm$ 2.0	2.5 $\pm$ 0.2	0.9 $\pm$ 0.1	2.6 $\pm$ 0.2

// = laminated   CS = coating speed   SiO$_x$ LT = SiO$_x$ layer thickness $\Delta Q/\Delta t$ = permeation rate   LT = lag time P = permeation coefficient D = diffusion coefficient S = solubility coefficient   [a]each value is the mean of four measurements ($n = 4$)   [b] SD value.

sus an average of $7.6 \times 10^{-10}\,\mathrm{g\,cm^{-2}\,s^{-1}}$ for SiO_x coated PET film, an increase in barrier properties of the latter by a factor of ~ 3 times is obtained at $35\,^\circ C$ (Table II). A respective increase in lag time was observed from $47.3 \times 10^3\,\mathrm{s}$ (13 h) for the uncoated film to $87.8 \times 10^3\,\mathrm{s}$ (24.4 h) for the SiO_x-coated film. Accordingly based on an average permeation rate of $61.5 \times 10^{-9}\,\mathrm{g\,cm^{-2}\,s^{-1}}$ for uncoated PET film versus an average of $2.8 \times 10^{-9}\,\mathrm{g\,cm^{-2}\,s^{-1}}$ for SiO_x-coated film, an increase in barrier properties of the latter by a factor of ~ 26 times is obtained (Table III) at $45\,^\circ C$. A respective increase in lag time was observed from $18.2 \times 10^3\,\mathrm{s}$ (5 h) for the uncoated film to $23.3 \times 10^3\,\mathrm{s}$ (6.5 h) for the SiO_x-coated film.

What is interesting to note is the increase in the permeation rate of both the uncoated and SiO_x-coated PET film by approximately one order of magnitude for a temperature increase equal to $10\,^\circ C$. Respectively lag times for both the uncoated and the SiO_x-coated PET films increased by a factor of 3 for a temperature increase equal to $10\,^\circ C$. This is of primary importance in commercial food packaging applications where a fluctuation in temperature by $10\,^\circ C$ *i.e.* during the summer months may result in a tenfold rate loss of the aroma of a particular packaged foodstuff.

Comments regarding permeation, diffusion and solubility coefficients in Tables II and III are analogous to those made for Table I. Comparing diffusion coefficient values for a given material at various temperatures, it is clear that diffusion is higher at high temperatures. On the other hand the solubility coefficient is more temperature independent and should decrease slightly at higher temperatures.[14]

Present permeation data are two orders of magnitude higher than those of Kontominas (1985) who reported a permeation rate for MEK of 8.4×10^{-13} $\mathrm{g\,cm^{-2}\,s^{-1}}$ through a two side PVdC coated PP film at a driving force of 100 ppm. Difference in permeation rate may be attributed to differences in driving force and the nature/thickness of the composite material tested.

Adamantiadi *et al.* (2001) reported permeation rates

Table IV. Activation energy (E_A) for permeation of MEK through uncoated PET, SiO_x-coated PET and SiO_x-coated PET// LDPE films at $2 \times 10^2\,\mathrm{cm\,s^{-1}}$ and $4 \times 10^2\,\mathrm{cm\,s^{-1}}$ coating speeds

Material	CS ($10^2\,\mathrm{cm\,s^{-1}}$)	E_A ($\mathrm{kJ\,mol^{-1}}$)
uncoated PET	—	85.90
PET–SiO_x	2	132.4
PET–SiO_x	4	126.5
PET–SiO_x//LDPE	2	137.8
PET–SiO_x//LDPE	4	133.7

// = laminated   CS = coating speed

between 2.55 and $10.2 \times 10^{-12}\,\mathrm{g\,cm^{-2}\,s^{-1}}$ for ethyl acetate through the same above packaging materials at a driving force of 600 ppm. These values are one order of magnitude lower than values reported in this work and may be attributed to differences in nature of the permeant molecule as well in driving force.

Activation energy values for permeation of MEK through uncoated PET, SiO_x-coated PET and SiO_x-coated PET films laminated to LDPE are given in Table IV.

Differences in activation energy values between uncoated and SiO_x-coated PET films (85.90 *vs.* $129.5\,\mathrm{kJ\,mol^{-1}}$) reflect the additional energy required for MEK to penetrate the glassy SiO_x matrix. Activation energy values for permeation of ethyl acetate through SiO_x-coated PET films equal to 97.21 $\mathrm{kJ\,mol^{-1}}$ were reported by Sajiki (1991). Giacin and Hernandez (1996) also reported activation energy values between 104.8 and $116.9\,\mathrm{kJ\,mol^{-1}}$ for permeation of ethyl acetate through acrylic coated OPP and between 142.5 and $148.3\,\mathrm{kJ\,mol^{-1}}$ for permeation of toluene through PVdC coated OPP. An activation energy value of $85.90\,\mathrm{kJ\,mol^{-1}}$ for permeation of MEK through uncoated PET seems to be high when compared to the activation energy of oxygen gas through PET below T_g ($E_A = 33.52\,\mathrm{kJ\,mol^{-1}}$). A possible explanation for this is that the molecular size of MEK is larger than oxygen and therefore requires a higher activation energy for permeation.

Table V. Oxygen permeation rates (OPR) of uncoated PET, SiO_x-coated PET and SiO_x-coated PET//LDPE films as a function of temperature and coating speed

Material	CS ($10^2\,\mathrm{cm\,s^{-1}}$)	OPR		
		$25\,^\circ C$	$35\,^\circ C$ ($10^{-8}\,\mathrm{cm^3\,cm^{-2}\,s^{-1}\,atm^{-1}}$)	$45\,^\circ C$
uncoated PET		$12.6^a \pm 0.8^b$	20.7 ± 1.8	24.5 ± 2.0
PET–SiO_x	2	0.3 ± 0	0.5 ± 0	0.6 ± 0
PET–SiO_x	4	0.4 ± 0	0.6 ± 0.1	0.7 ± 0.1
PET–SiO_x//LDPE	2	0.4 ± 0	0.6 ± 0.1	0.8 ± 0.1
PET–SiO_x//LDPE	4	0.5 ± 0	0.9 ± 0.1	1.3 ± 0.1

// = laminated   RH = 0%   CS = coating speed   [a]each value is the mean of four measurements ($n = 4$)   [b]SD value

Permeation to Oxygen

Table V gives oxygen permeation rates for uncoated, SiO_x coated and SiO_x-coated/laminated PET film as a function of temperature and coating speed. The oxygen barrier of the PET film increased by a factor of 40 times when coated with SiO_x at all temperatures. Differences in barrier properties of SiO_x-coated PET films with regard to permeation of MEK and oxygen can be explained by the significantly smaller size of oxygen as compared to MEK. The oxygen barrier remained in the same order of magnitude after lamination, indicative of the poor barrier of LDPE to oxygen. Coating speed did not significantly affect oxygen permeation rate. Norton (1961)[21] reported permeability for vitreous silica (thickness 0.27 nm) of 2.8×10^{-16} mol cm^{-2} s^{-1} atm^{-1}. This corresponds to a value of 2.09×10^{-9} cm^3 cm^{-2} s^{-1} atm (25 °C) for a thickness of ~90 nm (average thickness of SiO_x coating in the present study). Comparison of this value to an average value of O_2 permeation rate of 3.8×10^{-9} cm^3 cm^{-2} s^{-1} atm for SiO_x-coated PET films in the present work implies a rough increase in O_2 permeation by a factor of 2 owed to cracks on the SiO_x experimental coating as compared to the continuous matrix of the vitreous silica.

Permeation of Water Vapor

Table VI gives water vapor permeation rates for uncoated, SiO_x-coated and SiO_x-coated/laminated PET films as a function of temperature and coating speed. The water vapor permeation rate of the PET increased by a factor of 7–8 times when coated with SiO_x at all temperatures. This is in good agreement with MEK permeation data. The water vapor barrier of the SiO_x–PET further increased after lamination to LDPE by a factor of 6–7 but remained within the same order of magnitude as that of SiO_x-coated PET, a trend also shown for oxygen transmission. The slight increase in water vapor barrier properties of the coated and laminated PET film as compared to the coated PET film may be attributed to the very good water vapor barrier properties of polyethylene even though the "critical"

barrier in the present case is the SiO_x coating.

The higher coating speed (4×10^2 cm s^{-1}) resulted in a water vapor permeation rate (WVPR) about 1.5 to 2 times higher than at lower coating speeds, at all temperatures, but remained within the same order of magnitude as those of the lower coating speed (2×10^2 cm s^{-1}). The reason for this is unclear. When however SiO_x-coated PET films were subsequently laminated, differences in WVPR at the lower and higher coating speed were diminished due to the very good water vapor barrier properties of LDPE.

Present oxygen and water vapor permeation rate values are in good agreement to those in the literature[22] reporting oxygen permeation rate values of 1.5 cm^3 m^{-2} day^{-1} atm^{-1} (1.74×10^{-9} cm^3 cm^{-2} s^{-1} atm^{-1}) at 25 °C and RH = 70% for SiO_x-coated PET and 0.5 cm^3 m^{-2} d^{-1} atm^{-1} (0.58×10^{-9} cm^3 cm^{-2} s^{-1} atm^{-1}) for SiO_x-coated PET/laminated to CPP, 60×10^{-4} cm in thickness. The same author reported a water vapor permeation rate of 1.2 g m^{-2} d^{-1} (1.39×10^{-9} g cm^{-2} s^{-1}) at 40 °C and RH=100% for SiO_x-coated PET and 0.5 g m^{-2} d^{-1} (0.58×10^{-9} g cm^{-2} s^{-1}) for SiO_x-coated PET/laminated to CPP, 60×10^{-4} cm in thickness.

Barrier properties of present experimental materials as compared to conventional aluminum coated PET film (O.D. = 2.4), 5 cm^3 m^{-2} d^{-1} atm^{-1} (5.79×10^{-9} cm^3 cm^{-2} s^{-1} atm^{-1}) *vs.* 2 cm^3 m^{-2} d^{-1} atm^{-1} (2.31×10^{-9} cm^3 cm^{-2} s^{-1} atm^{-1}) for oxygen and 1.5 g m^{-2} d^{-1} (1.74×10^{-9} cm^3 cm^{-2} s^{-1}) *vs.* 0.7 g m^{-2} d^{-1} (0.81×10^{-9} g cm^{-2} s^{-1}) for water vapor, are of the same order of magnitude and thus the SiO_x coating provides an equivalent protection of packaged foodstuffs to that of the Al coating.

A point that should be stressed with regard to present permeation parameter values to MEK is that a driving force of 720 ppm w/v used throughout the experimental work is significantly higher than that to be expected in actual commercial food packaging applications. Thus under realistic conditions substantially lower permeation rate values to flavor compounds should be expected.

Table VI. Water vapor permeation rates (WVPR) of uncoated PET, SiO_x-coated PET and SiO_x-coated PET//LDPE films as a function of temperature and coating speed

Material	CS (10^2 cm s^{-1})	WVPR		
		25 °C	35 °C (10^{-9} g m^{-2} d^{-1})	45 °C
uncoated PET		$22.7^a \pm 1.9^b$	48.8 ± 4.1	64.1 ± 5.1
PET–SiO_x	2	2.9 ± 0.3	5.8 ± 0.4	9.0 ± 0.7
PET–SiO_x	4	3.6 ± 0.4	6.9 ± 0.5	11.6 ± 0.9
PET–SiO_x//LDPE	2	0.4 ± 0	0.8 ± 0.1	1.0 ± 0.1
PET–SiO_x//LDPE	4	0.5 ± 0	1.0 ± 0.1	1.2 ± 0.1

// = laminated   RH = 100%   CS = coating speed   [a]each value is the mean of four measurements (n = 4)   [b]SD value.

In conclusion experimental SiO$_x$-coated PET films as well as SiO$_x$-coated and laminated to LDPE, PET films show good barrier properties to both MEK and water vapor and excellent barrier properties to oxygen. Temperature seems to play a significant role in the permeation of MEK, increasing its transmission by approximately two orders of magnitude between 25 and 45 °C. The effect of temperature in oxygen and water vapor transmission is less pronounced. The coating speed does not seem to significantly affect barrier properties of experimental films.

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